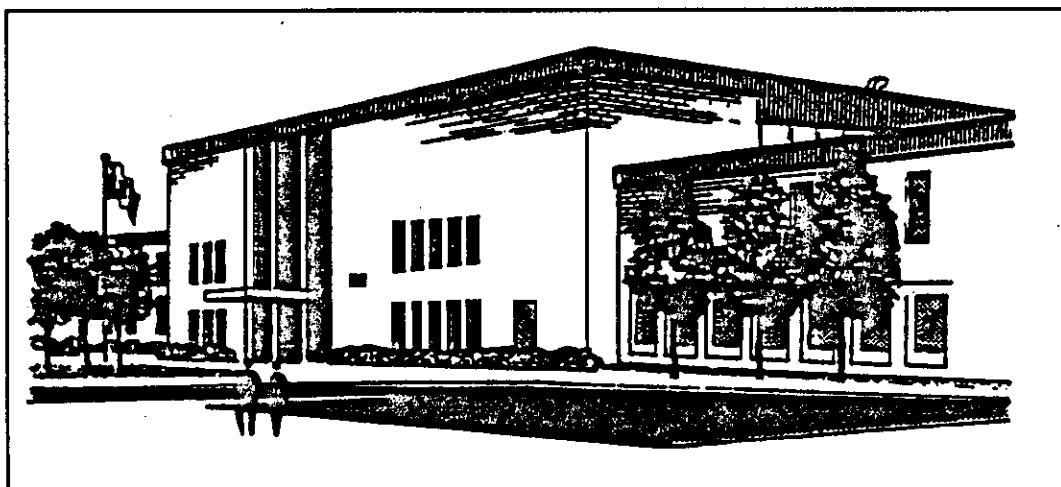


STUDIES OF THE DISSOLUTION AND LONG TERM WEATHERING OF SPILLED CRUDE OIL



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STUDIES OF THE DISSOLUTION AND LONG TERM WEATHERING OF SPILLED CRUDE OILS

by

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1. INTRODUCTION

There is a continuing concern about the short and long term effects of crude oil spills in the marine environment. The spilled oil is subject to evaporation, dissolution, emulsification into both water-in-oil and oil-in-water emulsions and it may be chemically transformed by chemical processes (notably photolysis) and by biodegradation. Two aspects of oil spill behaviour are of particular interest, because they are important both ecologically and economically.

First is the issue of the long term behaviour of the oil, for example whether it becomes dispersed or forms non-dispersible "pancakes" or tar balls, and how long the oil can survive on the ocean surface. It is suspected that some oils may be capable of sinking or prolonged submergence because of their inherent high density and their tendency to pick up diatomaceous material. Oil which survives on the sea surface, is likely to reach shorelines and can cause contamination of the intertidal region, resulting in high clean-up costs. It is thus important to establish experimental techniques or protocols by which the likely long term behaviour of an oil can be investigated under controlled laboratory conditions. A major focus of this project was to devise and test such a technique and protocol.

The second issue is the assessment of the concentration of dissolved hydrocarbons in the water column under an oil slick. This is important because dissolved hydrocarbons are believed to be a major contributor to the toxicity of oil spills as experienced by marine organisms such as fish. Experimental measurement of these dissolved concentrations is difficult because they are typically only a few parts per million of hydrocarbons, thus contamination of sampling equipment from the slick itself is a major problem. The use of sample bottles is often unreliable because the bottle must be passed through the slick or a sheen. The use of tubing through which the water is pumped and continuously analyzed by techniques such as fluorescence has proved successful, but there are concerns that the hydrocarbon may be sorbed on the tubing walls. It is noteworthy that the hydrocarbons found in dissolved state in the water tend to be those of low molecular weight and aromatic character. Indeed, benzene and toluene alone often contribute over half the total. These hydrocarbons are also volatile, which has enabled head space or "purge and trap" analysis to be used for their determination. This technique is very attractive because

the air-water partition coefficients of these substances usually exceed 0.1 thus air is a fairly efficient "extractant". These considerations lead to a suggestion that *in situ* head space analysis may be a feasible method of determining hydrocarbon concentrations in the water under a slick.

The challenge is then to devise a system by which the water under the slick can be contacted with air to achieve air-water equilibrium with the air being analyzed for its hydrocarbon content. Since *in situ* analysis is difficult, it may be preferable to trap the hydrocarbons present in a sample of air and determine the amount trapped by a later thermal desorption step with subsequent gas chromatographic analysis. This task was addressed in this project. A prototype system was designed, tested, modified and further tested. At this stage the objective was to establish the feasibility of the approach rather than devise a fully operational system.

In summary, the aims of this project were (1) to devise a laboratory system or protocol which can be used for the study of the long term behaviour of oil on the ocean surface and (2) to design and test systems which can be used to determine the concentration of dissolved hydrocarbons in water at the parts per million level by head space analysis *in situ*. This report is structured to treat these tasks separately with accounts of the experimental work, the results obtained and discussion of the results. Conclusions and recommendations are also presented at the end of each section.

2. LONG TERM WEATHERING STUDIES

2.1 Systems Development

Several systems have been developed in the past which could be used or adapted for the present purposes. From an extensive examination of their operating characteristics, criteria were developed which were applied to the selection of the system:

- ♦ A sample of oil has to be maintained, observed and sampled on the surface of water of desired salinity in contact with air for a period of weeks.
- ♦ The air and water flow conditions or turbulence should be controllable.
- ♦ Temperature should be controlled, but variable as desired.
- ♦ It should be possible to subject the oil to photolysis under controlled conditions.
- ♦ Conditions should be such that "mousse" formation occurs.
- ♦ A high degree of reproducibility is desired.
- ♦ The system should be reasonably inexpensive and compact so that a number of replicates can be operated.
- ♦ The system should be sufficient robust and reliable that it can be operated 24 hours per day with only periodic inspection and supervision.

A considerable number of systems were devised and tested. A primary concern was how motion or turbulence could be imparted to the system. An attractive approach is the use of an air stream to drive the oil over a water surface thus simulating oceanic conditions as is done in the Mackay-Nadeau-Steelman (MNS) dispersant test. (Mackay and Szeto, 1980) The main difficulty was that on prolonged exposure oil tends to adhere to the vessel walls.

An oscillating hoop system was tested in which a hoop is oscillated at the air-water interface causing the oil inside the hoop to be driven by wave action and drift to the centre. The main difficulty is the mechanical complexity of the oscillating system which results in periodic breakdown. Noise is also a nuisance.

A system was devised in which water was pumped to and from a cylindrical vessel creating a swirling motion which tended to trap the oil at the centre away from the sides. It was

found that occasionally oil was drawn into the pump and was dispersed. This was remedied in a subsequent version by locating the pump impeller in the vessel, thus avoiding the possibility of leaking tubing, but leakage problems were encountered with the gland through which the impeller was driven.

In general, it appeared that the most promising system involved water swirling in a bowl-shaped vessel. It was then suggested that rather than swirl or rotate the water, the bowl and contents should be rotated. Various configurations were investigated. A simple and very reliable method was to place a bowl of water on a gramophone turntable and rotate it at 33 rpm. The water surface then adopted a concave parabolic shape (as is discussed later) with the oil tending to locate in the depression away from the walls. This system has the attractive feature of mechanical simplicity because there are no pumps or agitators. The problem was that the oil was quiescent on the water surface, i.e. there was no oil-water agitation. This was solved by inserting a stationary "stirrer" into the water, thus inducing turbulence. Fig. 2.1 shows the principle.

A major benefit of this stirrer was that it could be located and shaped such that it tended to drive the oil towards the centre of the bowl thus reducing the tendency for the oil to reach the edge of the bowl. It acted rather like a plough on the water surface creating dispersed (oil in water) drops.

Several configurations were tested of various diameter, rotation speed, vessel shape and stirrer locations and a "final" design was selected for more detailed testing. The primary advantages of this system are that it can be assembled from relatively inexpensive parts, it is mechanically simple and robust, the water surface is readily observable, it can be subjected to additional wind agitation and photolysis, and samples can be taken as desired. The system is described in the next section (2.2) and observations and results are presented in section 2.3. It is entirely possible that another superior system could be devised but the proposed system has many appealing features and is, we judge, worthy of more extensive evaluation. In the interests of brevity, the large number of unsuccessful or partially successful tests conducted during the exploratory phase are not described. Only the final versions are discussed.

2.2 Prototype System

A novel apparatus which rotated a vessel containing the oil in a salt water solution on a gramophone turntable was devised and used in the study of long term weathering of crude oils. The design of the apparatus resulted from several months of experimentation and planning.

Weathering Apparatus

The apparatus consisted of a one speed, one horsepower motor which rotated a plexi-glass circular vessel at 33 rpm. A second glass vessel (190 mm diameter x 100 mm height) containing the oil and salt water was positioned inside the vessel; foam was inserted between the two vessels to correct for the differences in diameter. A stationary stirrer (1.5 cm x 1.5 cm x 1 mm) angled at 15° was inserted into the oil/water system to induce turbulence and oil-water agitation. A schematic drawing of the apparatus is shown in Fig. 2.1.

Approximately 15 mL of either EPS standard, Kuwait Crude, Prudhoe Bay Crude or California Crude API 15 oils was combined with 1 L of salt water (3% by weight NaCl).

After the salt water solution was placed in the pyrex glass vessel, the motor was switched on. When the water surface had formed a parabolic shape, the oil was poured into the centre. Samples were extracted from the oil slick with a syringe after the first and second hours and thereafter in twenty four hour intervals. The run was completed and the oil slick collected once a stable water-in-oil emulsion was formed and there was no further apparent change to the oil.

The physics of the rotating bowl are relatively simple. When a cylindrical tank is filled with fluid and rotated in the radial direction, the water surface results in a parabolic profile. By the influence of centrifugal force, the water in the rotating bowl tends to accelerate towards the edge of the system while the less dense oil phase remains suspended in the centre. A shear force acting at the container/liquid interface sets the liquid in motion while the viscosity of the fluid itself determines the rate at which steady-state surface profile is attained. The final surface profile of the liquid has the form, (Archer, 1992)

$$y = (\Omega^2/2g) x^2$$

where, y = vertical displacement, (m)

Ω = radial velocity, (rad/s)

g = acceleration due to gravity, (9.81 m/s^2)

x = horizontal displacement from the centre, (m)

Four oils with different physical chemical properties were studied - EPS Standard, Prudhoe Bay Crude Oil, Kuwait Crude oil and California Crude AP1 15 Oil. Each oil sample was weathered until a stable water-in-oil emulsion was formed. Observations were recorded and samples were taken for analyses at twenty-four hour intervals. Evaporation of lower boiling hydrocarbons was the dominant weathering process; samples were evaluated for the extent and rate of evaporation using gas chromatography. Once a stable water-in-oil emulsion was formed, the water content of the emulsion was determined using the Karl-Fischer method and apparatus. The final results were analyzed to seek relationships between the physical and chemical properties of the oil and the properties of the emulsion.

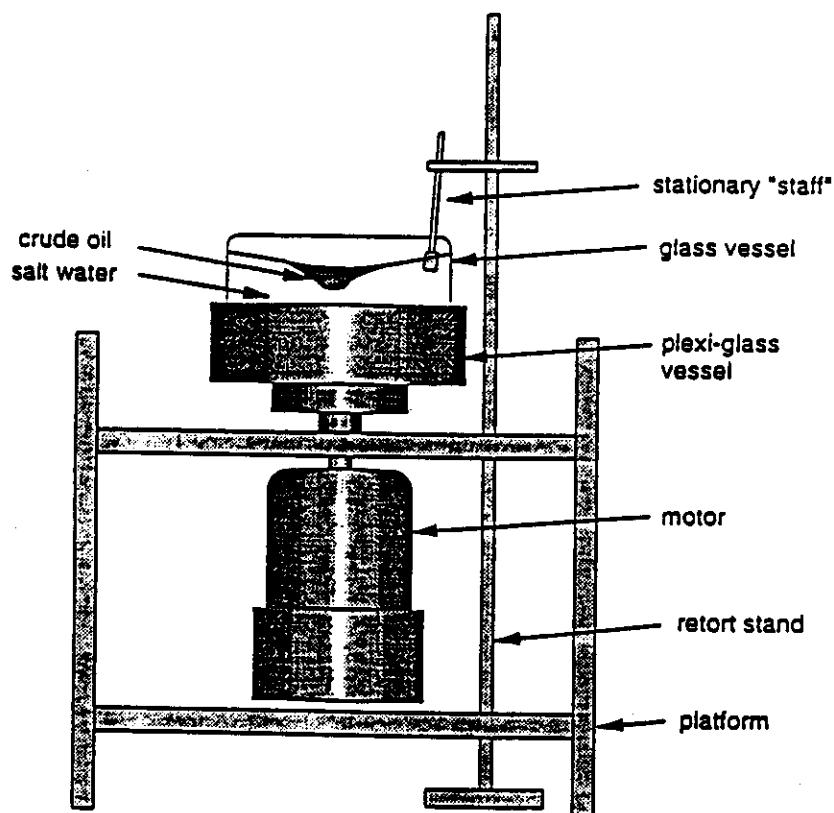


Figure 2.1 Rotating Bowl Apparatus

2.2.1 EXPERIMENTAL

Karl-Fischer Titration for Water Content of the Oils

A Karl-Fischer accessory model 392 titrator with an automatic burette, model 395 was used to determine the water content in each of the water-in-oil emulsions formed.

The Karl-Fischer reagent was supplied by Caledon Laboratories Ltd and had the following composition:

Diethylene glycol monomethyl ether > 70%

Imidazole 10-30%

Iodine 5-10%

Sulfur dioxide 10-30%

The solvent was initially a 50/50 mixture, by volume, of chloroform (100% pure) and methanol (99.8% pure).

In later experiments the emulsion samples were first dissolved in a mixture of toluene and methanol (80% and 20% respectively) as opposed to injecting the pure emulsion directly into the titration vessel. Dissolving the samples eliminates the problem of oil/water separation inside the needle of the syringe. It also allows for larger sample sizes and thus reduces the variability inherent with small sample sizes.

Once the power was initiated, the syringe/burette automatically filled up with the reagent. The beaker into which the sample was placed was filled with enough solvent to submerge the electrodes, ie. about 100mL. The solvent had to be titrated before the oil sample was injected because it was continually reacting with the air, producing water. The titration was completed when the endpoint of 20 μ A was reached; there was a waiting time of 20 seconds. The sample of oil was then injected and the titrator reset to begin a new titration. The water content of the emulsion was determined by comparing the amount of reagent used to titrate the emulsion with the amount required to titrate a sample of water of known mass.

Toluene Distillation for Water Content of the Oils

The determination of water content was carried out as described in the ASTM D 4006 with a few minor modifications such as substituting toluene for xylene, as the solvent.

The calibration of the entire apparatus was achieved by adding known amounts of distilled water at 20°C, to 100 ml of dry toluene. The emulsion sample was weighed, placed in the 250 ml round bottom flask, and mixed with 100 ml of toluene. A magnetic stirrer was added and then the flask was attached to the distillation apparatus. Heat was applied slowly up to a temperature of 180 °C, as measured in the silicone oil bath. After distillation for approximately 1 hour, the heater was turned off and the water in the trap was allowed to separate from the toluene. Any water droplets that adhered to the inner surface of the water condenser, were flushed down into the trap by adding small amounts of toluene from the top of the condenser.

In the initial stages of the study, every emulsion sample was analyzed four times. Later, as the accuracy of this method was confirmed, the number of distillations was reduced to one.

Gas Chromatography

The oil samples were analyzed using open column chromatographic separation in a Hewlett Packard 5700A gas chromatograph. The glass capillary column, 0.75mm ID by 30m long, was coated with SPB-5, supplied by Supelco Canada. The peaks were recorded on a Shimadzu Chromatopac C-R1A integrator. The operating conditions were as follows: an initial temperature of 50°C was maintained for 8 minutes, increased at a rate of 5°C / minute until a final temperature of 220°C was reached and held for 30 minutes. The volume of an injected oil sample was 0.5µL.

2.3 Results

Results are presented in Table 2.1 which show the water content of the emulsions analyzed by both the Karl Fischer Titration and the Toluene Distillation method under various experimental conditions. Emulsions made from Kuwait Crude and Prudhoe Bay Crude were used for the analysis.

The toluene distillation method was used to monitor the change in water content of the emulsions with time. The results of these experiments are shown in Table 2.2. Although the Toluene Distillation method gave reproducible results, this method had the disadvantage of requiring a fairly large sample size (4 to 5 g) in order to give sufficient accuracy. This limited the number of measurements that could be performed on each emulsion. Another drawback was the length of time required to complete each analysis, namely 2 to 3 hours.

The accuracy of the Karl Fischer Titration was improved markedly by dissolving the emulsion sample in the toluene/methanol solution prior to injection into the titration vessel. Dissolving the emulsions in a solvent mixture allowed larger, more homogeneous samples to be injected, and therefore more reliable results of water content were obtained.

The main advantages of the Karl Fischer Titration compared to the Toluene Distillation were the shorter time to analyze a sample (15 minutes compared to 2 to 3 hours), and the relatively small sample sizes (0.2 to 0.3 g), that were required to obtain reproducible results. Figures 2.3 to 2.8 give gas chromatographs of the various oils at various stages of weathering in the rotating bowl apparatus. It is clear that the oil is evaporating as expected and that the system is capable of simulating evaporation on the ocean surface.

	Toluene Distillation	Karl Fischer Titration	Experimental Conditions
Kuwait I	66.1%	69.8%	1) stirrer: plastic spatula
	55.9%	68.4%	2) time of sampling:
	63.6%	65.0%	after 7 days
	64.9%	-----	3) separation of non-emulsified water:
	62.6%	67.7%	no
Kuwait II	55.7%	70.4%	1) plastic spatula
	63.2%		2) after 7 days
	65.1%		3) no
	70.0%	-----	
	63.5%	70.4%	
Kuwait III 1)	78.7%	84.5%	1) plastic knife
	80.0%	88.5%	2) after 7 days
	85.4%	-----	3) no
	81.4%	86.5%	
Kuwait III 2)	80.0%		1) plastic knife
	78.6%		2) after 7 days
	79.7%		3) yes
	79.4%		
Kuwait IV	77.5%		1) plastic knife
	79.4%		2) after 6 days
	78.5%		3) yes

Table 2.1 Water Content of Emulsions

Item (1) under "experimental conditions" refers to the stationary stirrer used and item (3) refers to whether or not there was separation of bulk water from the emulsion.

Table 2.1 continued

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	Toluene Distillation	Karl Fischer Titration	Experimental Conditions
Prudhoe Bay I	76.6%	73.2%	1) plastic knife
	75.0%	73.6%	2) after 7 days
	-----	72.0%	3) yes
	75.8%	72.9%	
Prudhoe Bay II	75.0%		1) plastic knife
	75.0%		2) after 7 days
	-----		3) yes
	75.0%		
California I		42.4%	1) plastic knife
		41.1%	2) after 1 day
		-----	3) no
		41.8%	

	Water Content	Time of Sampling	Experimental Conditions
Kuwait V	48.1%	after 24 hours	1) stirrer: steel spatula (1cmx22cm)
	61.3%	after 48 hours	2) separation of non-emulsified water: yes
	72.2%	after 72 hours	
Kuwait VI	76.7%	after 24 hours	1) stirrer: steel spatula (2.5cmx22cm)
	78.1%	after 48 hours	2) yes
	77.1%	after 72 hours	

Table 2.2 Water Content of Emulsions As A Function of Time

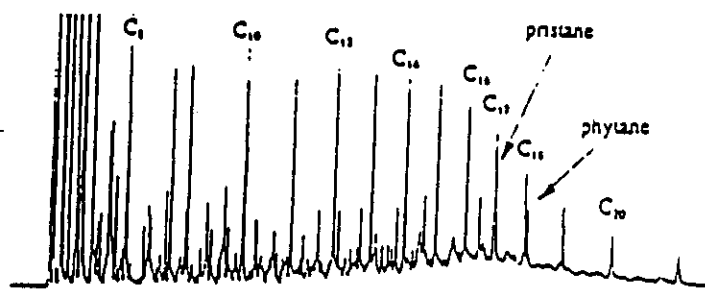
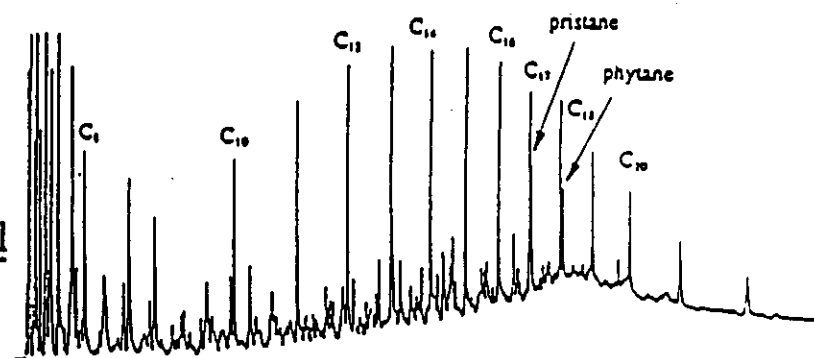
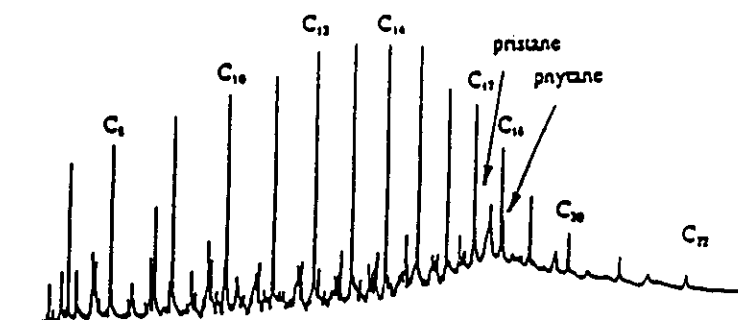
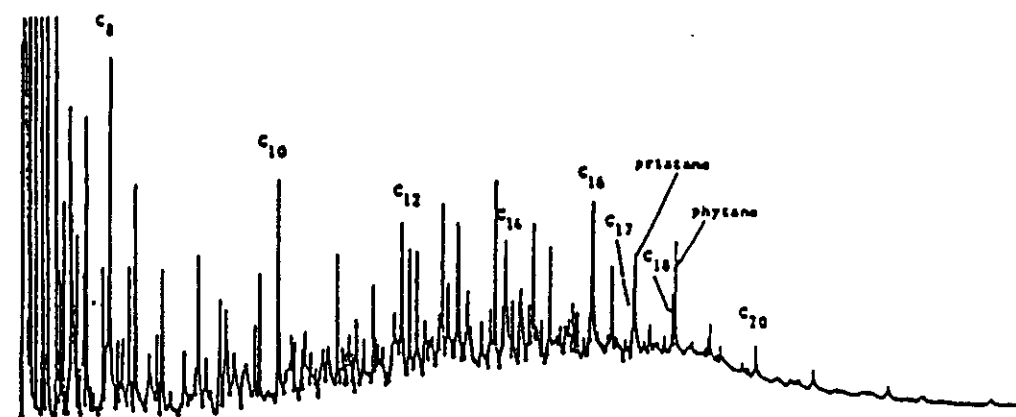
EPS Standard OilPrudhoe Bay Crude OilKuwait Crude OilCalifornia Crude Oil

Figure 2.2 Gas Chromatograms of Fresh Oils

Oil	Time to Form Stable Emulsion	Water Content (% by mass)	
		Fresh	Emulsion
EPS Standard	8 days	0.0135	58.7
			25.2
			13.4
			73.9
Kuwait Crude	3 days	0.0256	62.5
			62.4
			91.9
			88.8
Prudhoe Bay Crude	7 days	0.015	51.9
			8.5
			62.2
California Crude API 15	1 day	0.282	75.4
			25.2
			13.4
			73.9

Table 2.3 Water Content of Fresh and Emulsified Crude Oils

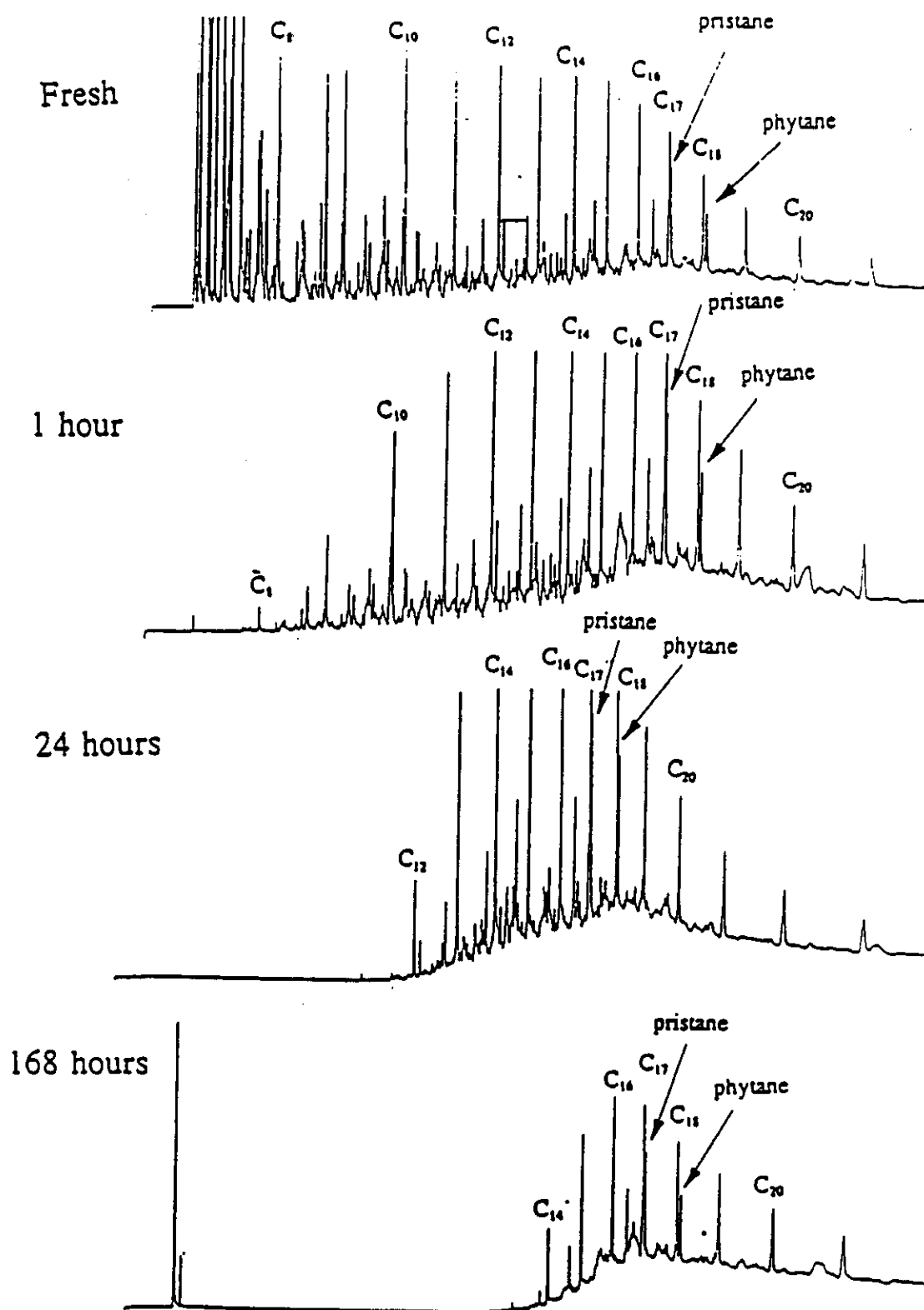


Figure 2.3 Gas Chromatograms of EPS Standard Oil

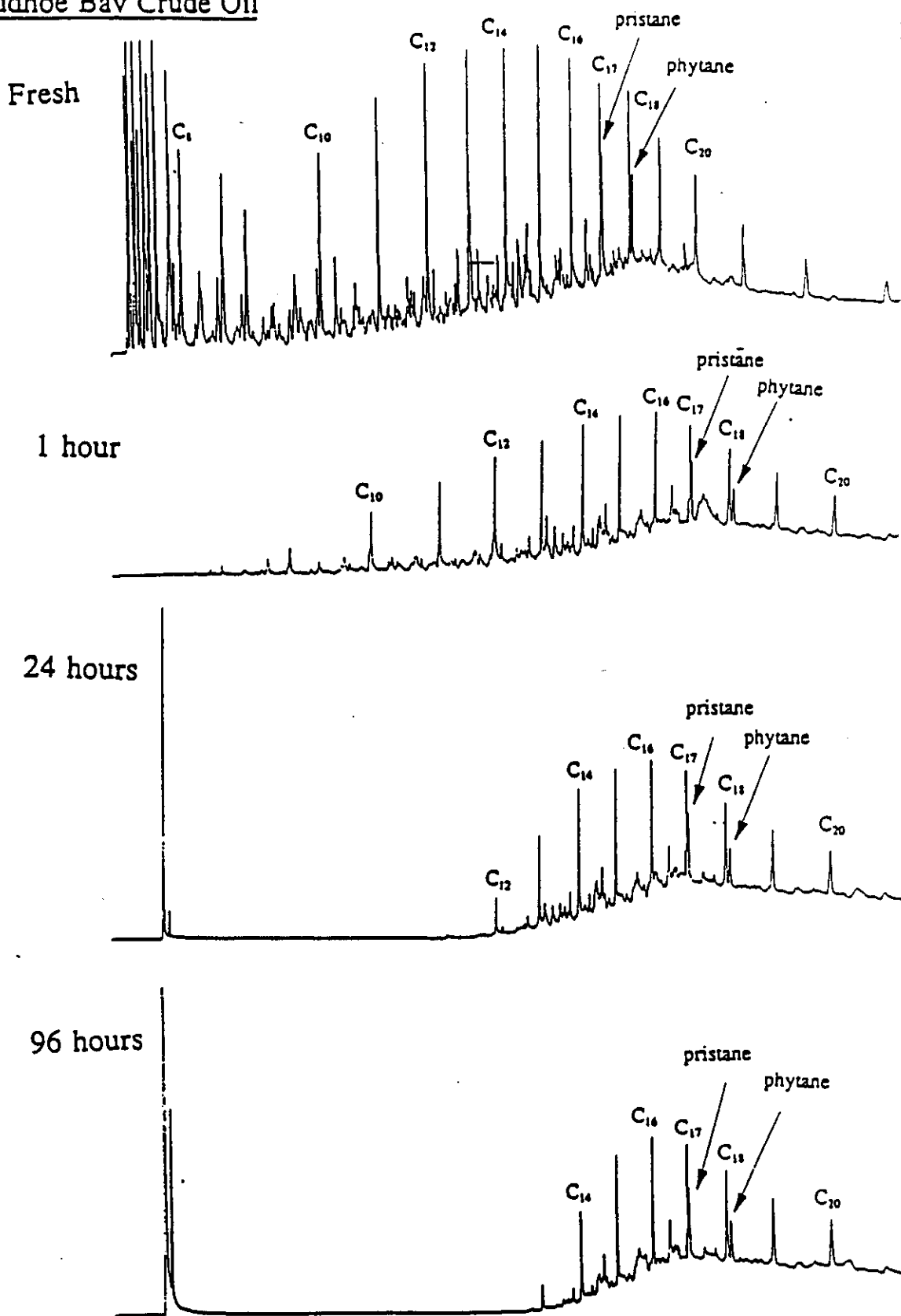


Figure 2.4 Gas Chromatograms of Prudhoe Bay Crude Oil

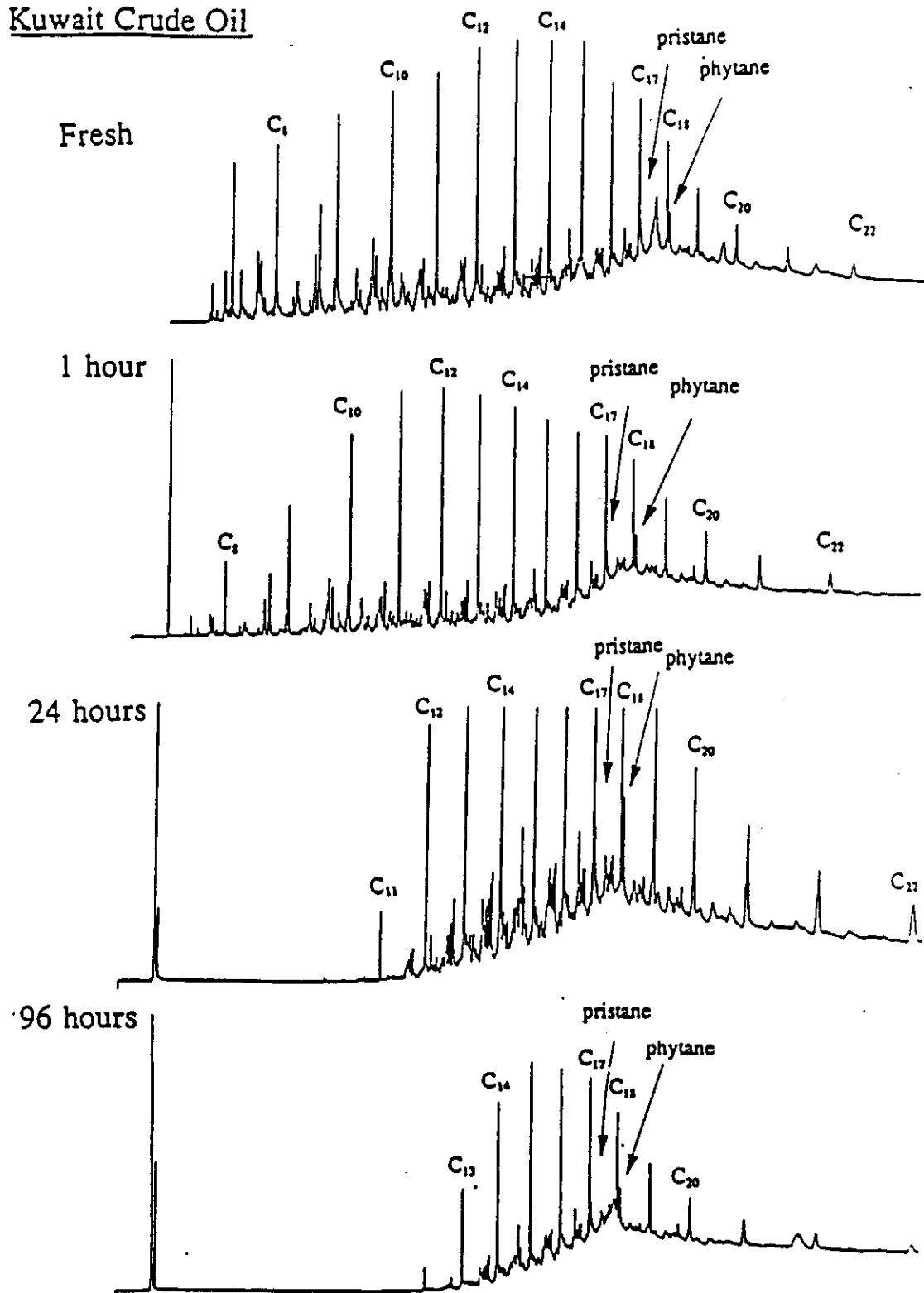
Kuwait Crude Oil

Figure 2.5 Gas Chromatograms of Kuwait Crude Oil

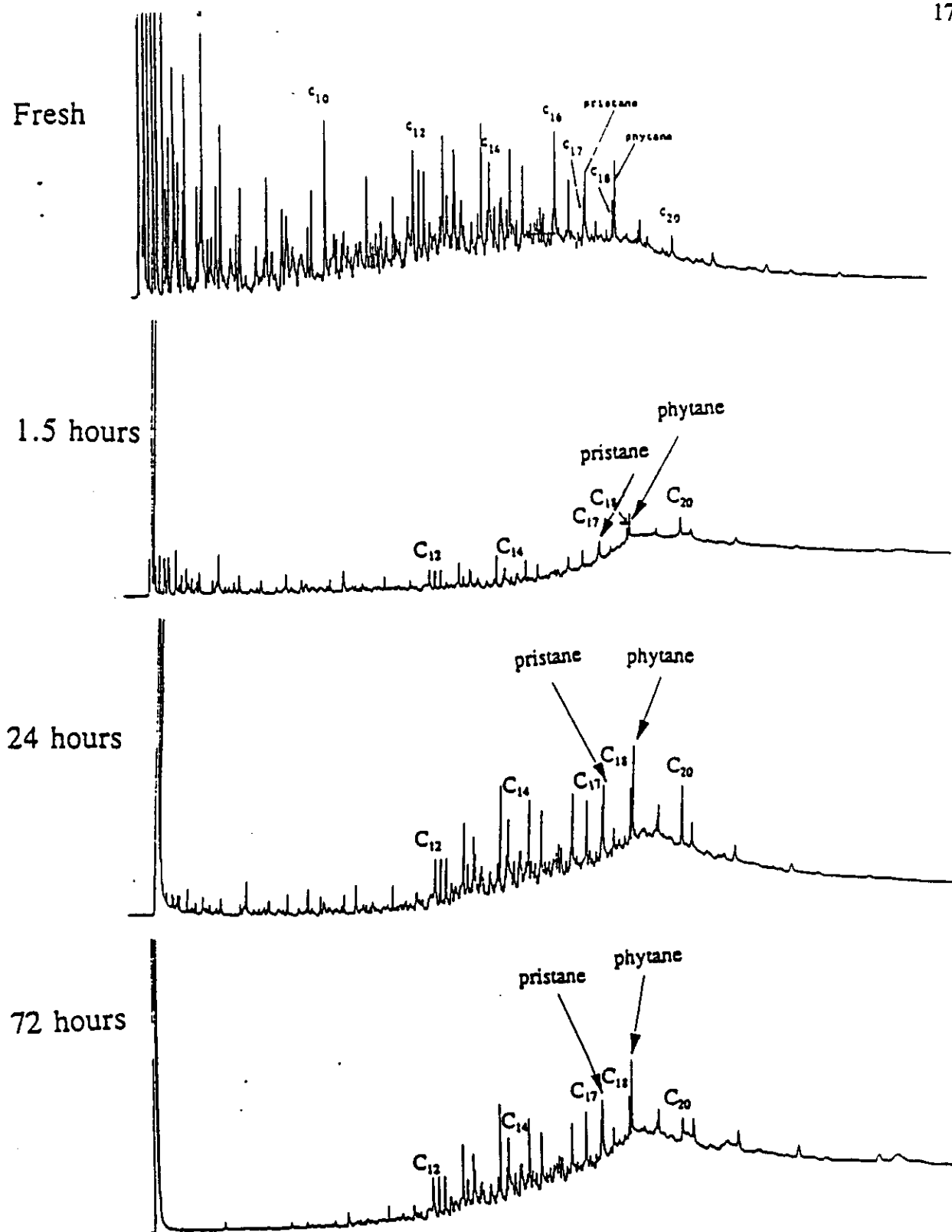


Figure 2.6 Gas Chromatograms of California Crude Oil

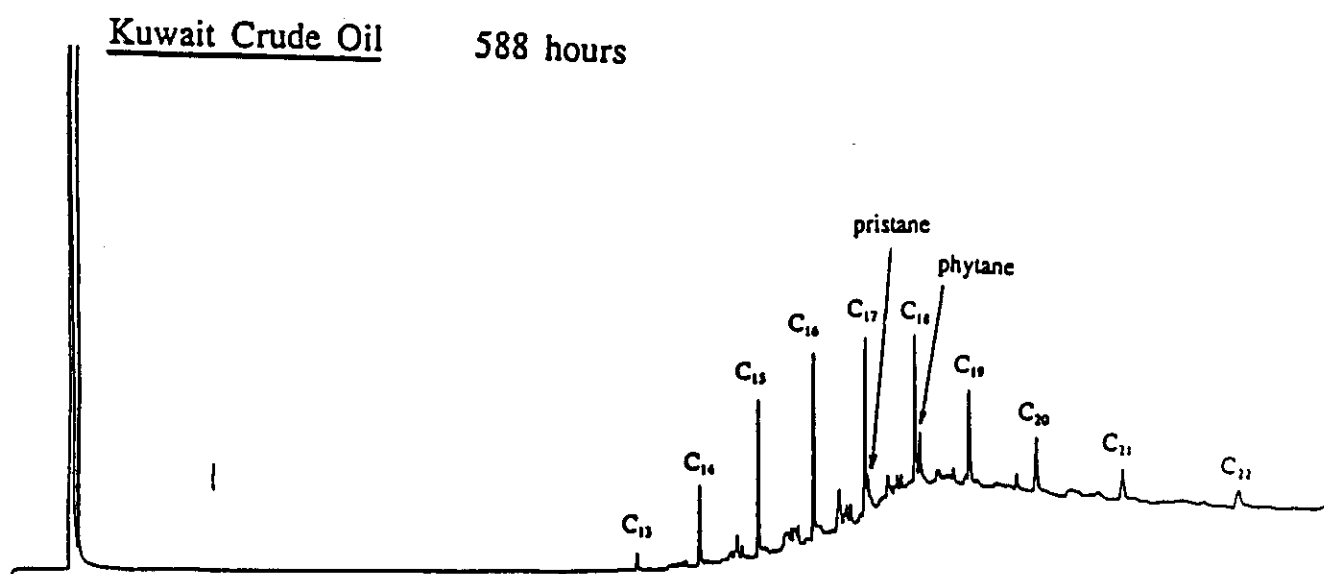


Figure 2.7 Gas Chromatogram of Weathered Kuwait Oil

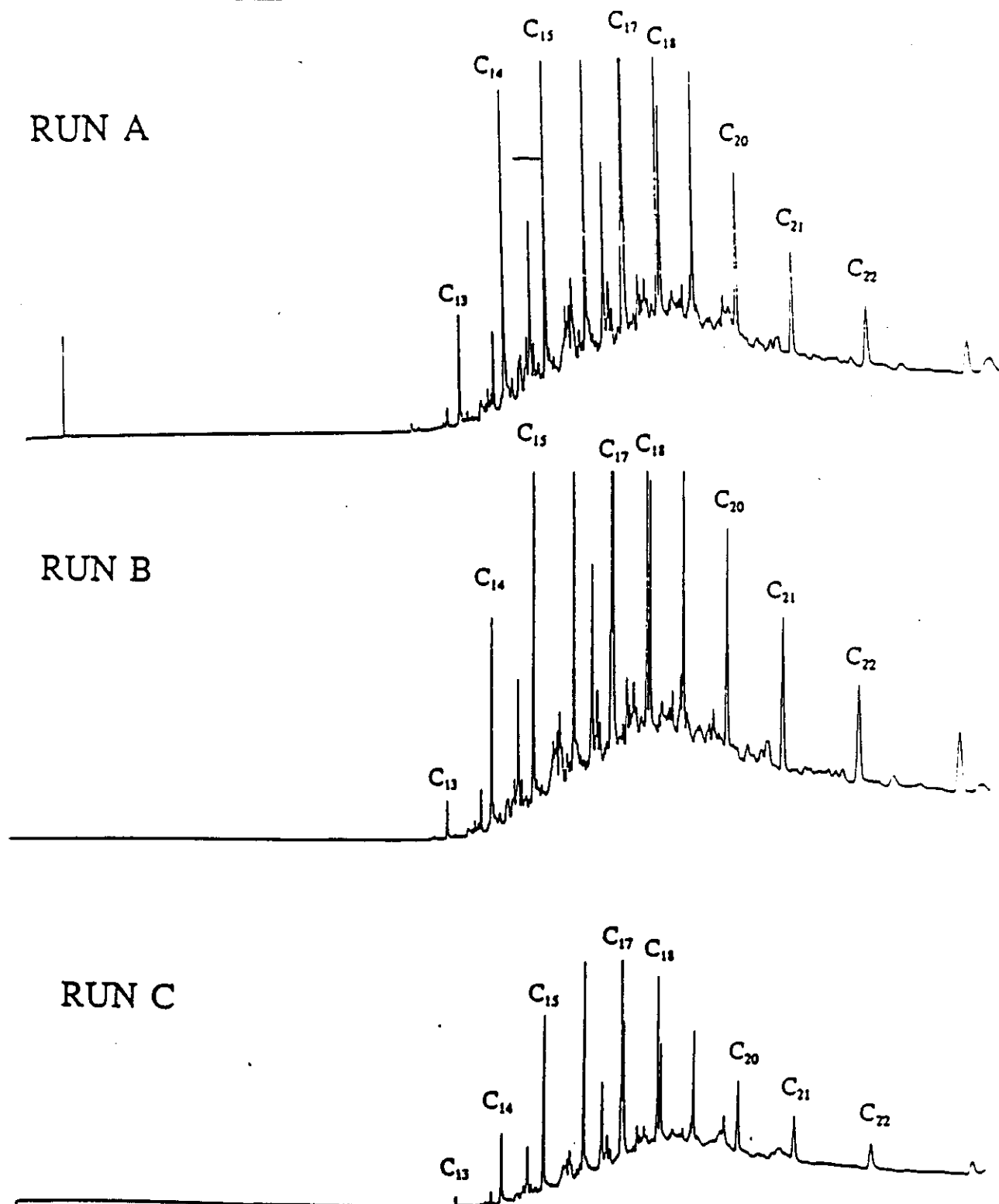


Figure 2.8 Gas Chromatograms of Weathered EPS Standard Oil

2.4 Discussion

Oil Properties

Oil is viewed as consisting of four main components: saturates, aromatics, polars and asphaltenes. Asphaltenes are the most complex group, have high molecular weights, ranging from 500 to 10000 g/mol, and range in carbon numbers from C_{30} upwards. They consist of condensed polycyclic aromatics material with heteroatoms (i.e. nitrogen, sulfur, oxygen, metal) with side aliphatic chains. Asphaltenes are a component of the interfacial film which develops between the water and oil phases facilitating the dispersion of water molecules into the oil phase. This phenomenon helps to stabilize water-in-oil emulsions.

The four oils used to study emulsions, in order of increasing viscosity, were EPS standard oil, Kuwait Crude oil, Prudhoe Bay Crude oil and California Crude API 15 oil. The properties of these oils are presented in Table 2.4. From the examination of gas chromatograms for the fresh oils, it was evident that all the crude oils except Kuwait (which had been weathered), contained a large proportion of volatile components. Gas chromatograms of the fresh oils are displayed in Fig. 2.2.

	California Crude API 15	EPS Standard	Kuwait Crude	Prudhoe Bay Crude
API	15	36.8	31.2	27.0
Density @20°C (g/mL)	0.9735	0.835	0.870	0.901
Dynamic Viscosity @15°C (cp)	6400	9.2	22.2	196
Hydrocarbon Group (weight %)				
saturates	13.7	84.2	54.3	78.3
aromatics	16.4	12.8	30.06	7.6
polars	25.8	1.2	17.9	2.5
asphaltenes	20.01	1.8	3.5	2.04
Wax Content (weight %)	1.6	6.93	3.9	3.86

Table 2.4 Oil Properties

Oil Weathering Processes

Evaporation is the first and most important weathering process that occurs when oil is spilled and comes into contact with water. It is the process by which the light ends (the more volatile components) evaporate leaving a residue which has a higher specific gravity and viscosity than the original oil. The rate and extent of evaporation depend upon the physical and chemical properties of the components of the particular crude oil, wave action, wind velocity and water temperature. Simulated weathering tests in the laboratory showed that virtually all fractions lighter than C_4 (referred to as the volatile components) evaporated within the first hour independently of the type of oil used. After the second hour, C_4 had also evaporated and after twenty four hours, only fractions higher than C_{12} remained. Since all the volatile, and some of the moderately volatile components had already evaporated, the rate of evaporation decreased significantly after the first twenty four hours. These trends are illustrated in figures 2.3 to 2.6. The time required to form a stable water-in-oil emulsion was dependent on the physical chemical properties of the oils. In general, those oils with a higher viscosity and higher mass percentage of asphaltenes were observed to form emulsions more rapidly. EPS, for instance, which has the lowest mass percentage of asphaltenes (1.8 weight %) and the lowest viscosity, formed an emulsion in eight days. California Crude, on the contrary, which was the most viscous and contained the highest mass percentage of asphaltenes, formed a very stable emulsion in only one day. There appeared to be no relationship between the rate of emulsification and wax content.

Most of the oils become lighter in colour when an emulsion was formed. Prior to the formation of emulsion, when the oil is fresh and contains negligible amounts of water, it absorbs all incident light. When an emulsion is formed, the oil contains a substantially higher percentage of water. The water droplets are believed to reflect the incident light, thus the emulsion appeared to be lighter in colour. The water contents of fresh oil and emulsions are presented in Table 2.2.

Horizontal spreading of the oil is a function of both specific gravity and surface tension of water, the surface tension of water being higher than that of oil. The rate of spreading was observed to be retarded by the presence of an oil-in-water emulsion. Stability was also enhanced by evaporation of the lighter carbon numbers which are believed to help retain asphaltenes in solution. The remaining oil had a higher percentage of the high molecular weight compounds,

such as asphaltenes, which stabilize emulsions. It appears that evaporation of the more volatile components (probably the aromatics) induces precipitation of the asphaltenes.

General Observations of Oil Behaviour

Because of the centrifugal motion of the rotating vessel, all the oil samples formed concave shapes at the centre of the bowl.

EPS standard oil was the least viscous and the least dense of the four oils examined. It experienced minimal sticking to the sides of the glass vessel and the stirrer. During the first 48 hours, oil particles were dispersed from the main slick into the water column. The majority of these dispersed oil particles were located beneath the centre of the slick. There were many ellipsoid shaped "islands" or mini-slicks suspended in a thin film of oil which surrounded the main body. These mini-slicks became stable after few days of weathering and a stable emulsion was formed after eight days.

Prudhoe Bay Crude behaved similarly to EPS; oil particles were initially dispersed into the water column and ellipsoid "islands" were suspended in an oil film surrounding the main body of oil. The emulsion was formed in seven days and appeared to be more stable than that of the EPS.

Kuwait Crude oil also experienced minimal sticking to the side of the vessel and stirrer. Furthermore, suspended oil particles were observed in the water column. Fewer suspended oil particles were visible after twenty four hours. Instead, the oil formed a bulbous shape which almost touched the bottom of the vessel. This was apparently the result of the oil physically incorporating a body of water within its structure. A stable emulsion was formed in three days. The emulsion was very "mousse-like" and appeared to be much more stable than that of Prudhoe Bay Crude and EPS standard.

California Crude oil was the most viscous and contained the highest weight percent of asphaltenes. It immediately adhered to the sides of the vessel and the stirrer. The fresh crude was almost black with tar-like consistency. A stable concave shape formed almost instantaneously and a stable emulsion formed after one day.

Individual Oil Behaviour

California Crude API 15 oil was the most viscous of the four oils (6400 mPa.s) and contained the highest mass percentage of asphaltenes. It appeared to have formed a stable mousse after twenty four hours. The high viscosity appeared to retard horizontal spreading and caused the oil to immediately form a concave shape when it was poured in the vessel. Karl-Fischer titration indicated that the water content of the emulsion was only 20% by mass. The oil may have been so viscous that there was a very limited tendency for the oil to deform to accept more water. Aside from having a high mass percentage of asphaltenes, California Crude API 15 also has a large content of complex polar molecular compounds such as oxygen, nitrogen and sulfur. The combined presence of asphaltenes and polar compounds apparently served to increase the stability of the emulsion.

EPS, being the least viscous and least dense of the crude oils, took the longest time to form a stable emulsion. The relatively slow rate of emulsion formation was attributable to the fact that EPS had a large content of volatile hydrocarbons, which evaporated in the first twenty four hours, as well as to the low mass percentage of asphaltenes. As a consequence of its low viscosity, there was little resistance to horizontal spreading. Thus the oil spread quickly and tended to break up into "islands", even after a stable emulsion was formed. Instead, there was a film of oil on the surface of the water and numerous mini-slick which detached from the main slick. The water content in the emulsion ranged from 13.4% to 73.9%, with a substantial deviation from sample to sample. The reason for the wide distribution was that the water and oil have a strong tendency to separate into distinct phases when drawn into the syringe during the Karl-Fischer titration. After the excess water was discarded, the emulsion would again separate as it was injected into the apparatus. With the method employed, it was not possible to eliminate the phase separation. Due to the low viscosity of the oil and the absence of a high percentage of asphaltenes stabilizers, the emulsion was inherently unstable and could easily be disturbed by any shear force acting upon it. Prudhoe Bay Crude oil behaved in a similar manner to EPS largely due to the similarity in physical chemical properties and composition. Numerous mini-slicks were formed and a stable emulsion was formed in about a week. Both oils contained a high percentage of volatile components yet Prudhoe Bay had a higher density (0.911 g/mL vs 0.839 g/mL), a significantly higher viscosity (196 cp vs 9.2 cp) and a higher mass percentage of

asphaltenes (2.04% vs 1.8%). As a consequence of the higher density, higher viscosity and higher mass percentage of asphaltenes, the emulsion was more stable than that of EPS, with less separation and thus, more consistent results. The percentage of water in emulsion ranged from 8.5% to 75.4%, the average being on the higher end of the spectrum.

Kuwait Crude oil used in the experiment had already been weathered and thus contained a smaller fraction of volatile components. Kuwait crude oil behaved differently from the other oils. After the first twenty four hours, the oil had incorporated a volume of water with in the body of the slick, with the oil slick physically surrounded the water. Consequently, the slick was bulbous in appearance and almost touched the bottom of the vessel. This phenomena was still apparent when a stable emulsion had formed three days later. As with the other oils, when the emulsion was examined under a microscope, may tiny water droplets could be seen dispersed throughout the emulsion. With the exception of its high aromatic content, the properties of Kuwait crude oils were intermediate between the viscous California Crude API 15, the lighter EPS and Prudhoe Bay Crude oils. Similarly, its performance in the apparatus was also intermediate; no islands were formed, the viscous oil formed a stable emulsion in four days.

An experiment was conducted using Kuwait crude oil to study the long term effects of weathering. In time, the emulsion became very compact , containing no extraneous water and the surface was very light brown in colour. The emulsion appeared to be extremely viscous with almost no tendency to spread and the surface of the oil slick was a very light brown colour.

General Comments on Performance

This apparatus proved to be a successful for the study of evaporation and of the formation and weathering of water-in-oil emulsions. Its simple construction and design ensured that any mechanical failures would easily be rectified. The apparatus could also be left unattended for hours, although the water in the vessel had to be replenished ie. about 200 mL of distilled water were added each day. Five apparatus were run simultaneously to ensure consistent results; each oil was run a minimum of three times. The results proved to be consistent and thus the experiments were reproducible. This is illustrated in Fig. 2.8 which shows the chromatograms of EPS Standard oil for three different runs, each of which had been exposed to the atmosphere for 168 hours. Exposing the oil to the atmosphere not only resulted in evaporation but also

facilitated observation and made it possible to readily obtain samples. The apparatus was inexpensive to reproduce and compact, two apparatus required only 0.14 m² of space. During the period in which experiments were almost continuously conducted, no mechanical difficulties were encountered.

Some preliminary experiments were done to test the effect of photolysis using a simulated solar source. In view of the few results obtained, no detailed account of the findings is presented here, but it was apparent that the system could be used to investigate this important process. If desired, the rate of photolysis could be increased to accelerate natural rates.

Further Developments

The only major problem with the system was defining and controlling the degree of turbulence. It was difficult to position the stirring rods at exactly the same angle; different angles yielded differing amounts of turbulence, thus varying the time in which an emulsion was formed. In addition, the shape of the stirrer also had a substantial influence on both the degree of turbulence induced as well as the rate of emulsification. An ongoing experiment is designed to standardize the nature, shape, size and position of the stirrer in order to:

- (i) induce a controlled amount of turbulence to agitate water/oil contact as well as to help keep the oil from sticking to the sides of the vessel,
- (ii) to give easy access to the water column so samples can be taken from the water column without disturbing the surface profile of the water/oil system,
- (iii) to standardize the surface circulation pattern of the system so the results of the experiments are reproducible under "standard" conditions .

A series of experiment indicated that a thin flat metal plate with a larger surface area than the stirrer previously used had a potential of doubling the rate of emulsification. The larger surface area acted as a more efficient plough on the water surface, creating a higher intensity of dispersed (oil in water) drops. The metal plate was mounted to a thin hollow metal rod which allowed a long syringe to be inserted directed into the water column. This design makes it

possible to obtain samples from the water column without interference to the surface profile. This design is being subjected to further experimentation and verification.

A variable speed motor could eventually be used to determine the effects of increased turbulence on the rate of emulsification. Increasing the turbulence increases the water which comes in contact with the oil slick, most likely also increases the rate of emulsification. A long term experiment should be conducted to investigate the effects of other natural phenomena such as photolysis, rain, wind and dust, on the behaviour of the weathering oil. Photolysis can result in polymerization to form denser, higher molecular weight species and free radicals which are susceptible to oxidation resulting in the formation of denser oxygenated species such as peroxy and hydroxyl radicals, alcohols, ketones, carboxylic acid and aldehydes.

In addition, the effects of rain on the weathering of oil could also be studied by the application of simulated rain fall from a shower head. Rain increases the amount of water which comes in contact with the oil slick and would probably increase rate of emulsification.

The entire apparatus could also be enclosed in a temperature controlled chamber to investigate the effect of temperature.

Samples taken from the water column could be used to analyze the amount of oil dispersed and dissolved in the water column via dissolution. The lower molecular weight aliphatic and aromatic hydrocarbons as well as nonhydrocarbons tend to be removed from an oil slick by dissolution from the moment the oil is in contact with the sea water. An ongoing experiment uses a Purge and Trap Gas Chromatograph for water sample analysis. Fluorescence and Gas Chromatography/Mass Spectrophotometry can also be applied for water column analysis.

Liquid chromatography could be performed to determine the amounts of asphaltenes, aromatics, polars, saturates and waxes remaining at specific time intervals and a correlation between the composition of the oil and emulsion formation could be developed.

2.5 Conclusions

The work performed on the long term weathering of different crude oils and the study of oil-water emulsions using the prototype rotating bowl has resulted in the following conclusions.

1. The apparatus proved to be successful for studying the formation and weathering of water-in-oil emulsions. The nature, shape, size and position of the stationary stirrer have yet to be standardized to assure highly reproducible results.
2. Experimental results indicated that the more viscous oils ie. California Crude API 15, Kuwait Crude, formed emulsions more rapidly.
3. The water-in-oil emulsions formed by the more viscous oils were more stable.
4. Oils with a higher percentage of asphaltenes formed stable emulsions more rapidly.
5. The more volatile components in the oil, ie. C_4 and lighter, evaporated within the first hour.
6. The prototype rotating bowl has many appealing features and its success in studying the long term weathering of oil give it great potential for extensive evaluation. This apparatus should be used to study the effect of photolysis, rain, dust and temperature changes on the long term weathering of crude oil.

A systematic study is suggested in which various oils are subjected to weathering using various defined and reproducible levels of turbulence, as controlled by the stirrer design and configuration, at various temperatures, and subject to ranging degrees of photolysis. The oil and water should be subjected to analysis to determine compositional changes and emulsion formation.

Ultimately, it is desirable to "match" conditions in this system to oceanic conditions with a view to simulating these conditions more closely in the laboratory. It is hoped that it may be possible to simulate various sea states and wind conditions and establish a capability of accelerating the weathering process, for example achieving 4 days actual weathering in 1 or 2 days of laboratory time.

3. IN-SITU SAMPLING SYSTEM

3.1 Introduction and System Development

The only system which has been described in the literature which is related to this work is that of Sproule *et al.* (1991) which was modified by Murray and Andren (1991) to determine the concentration of dissolved hydrophobic, organo-chlorine chemicals, in the waters of the Great Lakes. Sproule's system is illustrated in Fig. 3.1. It is a cylindrical tube which floats at the water surface and is arranged such that air is bubbled through the water column and passed through a sorbent trap filled with a solid sorbent. The height of bubble rise is sufficient that there is nearly complete attainment of equilibrium between the bubbles and the water. After a known volume of air is passed through the system, the trap is removed and the adsorbed contents determined by thermal desorption. Holes in the cylindrical vessel ensure that the water is circulated, thus it is not appreciably depleted of hydrocarbons.

If the trap contents are determined (for example 10 mg of benzene) and the volume of air passed through the trap is known (e.g. 5 litres) then the concentration in the air can be deduced as $10/5$ or 2.0 mg/litre. If the air-water partition coefficient, K_{Aw} , is known (e.g. 0.25) then the water concentration can be deduced as $2.0/0.25$ or 8 mg/L.

Data are widely available which can be used to deduce K_{Aw} , an example being the compilations of Henry's Law Constants (HLC) by Mackay and Shiu (1981) and Mackay *et al.* (1992). It is clearly important to know the HLC accurately for the chemical in question at the temperature of interest and at the prevailing salinity.

The challenge in this situation is to devise a system which is submersible (as distinct from floating) in which a known volume of air can be contacted with water under conditions in which a high degree of approach to equilibrium is assured, and the hydrocarbons in that air are trapped and well preserved, free from contamination or loss, and then available for later analysis.

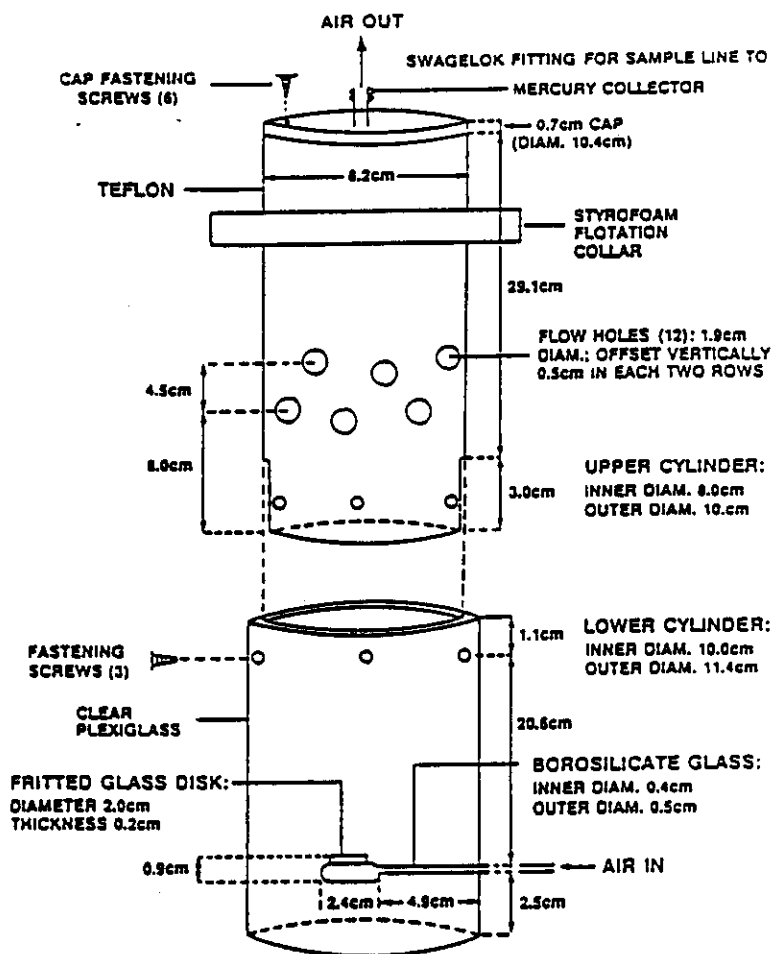


Figure 3.1 Sproule's System

3.2 System Development

A number of systems were suggested, designed, evaluated and modified. The principal difficulty is to ensure that the trap receives only air, with no possibility of contact with water, i.e. it must never "flood". It transpired that a key decision was whether the sorbent trap should be located on the sparger, i.e. submerged, or retained at the water surface connected to the sparger by a length of tubing.

For two reasons it was decided that the trap should be located beside the sparger. First, the use of a length of tubing raises the possibility that appreciable sorption may occur during the transit of the vapour stream from sparger to surface. Second, and more serious, if the trap is connected by an air column to the sparger, the base of that column will be at, or near,

atmospheric pressure while the surrounding marine environment will be at a higher (atmospheric plus hydraulic) pressure. This will cause a high and variable pressure difference to develop in the sparger valving or air-water separation system which could cause leakage and malfunction, especially if the system is deployed at considerable depths such as tens of metres.

Other aspects of the design which have some flexibility include whether to discharge the outlet air to the surface or more simply release it to the water by means of an inverted "U-tube". Both approaches have certain advantages. Lastly, there is still the question of the best method for providing air to the system, whether it should be introduced from the surface by means of a compressed cylinder or pump, or if it would be better to attach a compact compressed air cylinder which could deliver air to the sparger without the need for a long air inlet tube.

A prototype system was designed which, it is believed, is capable of successful operation for the desired purposes. (Fig. 3.2) Tests were performed on this device and the results are presented and discussed in the following section.

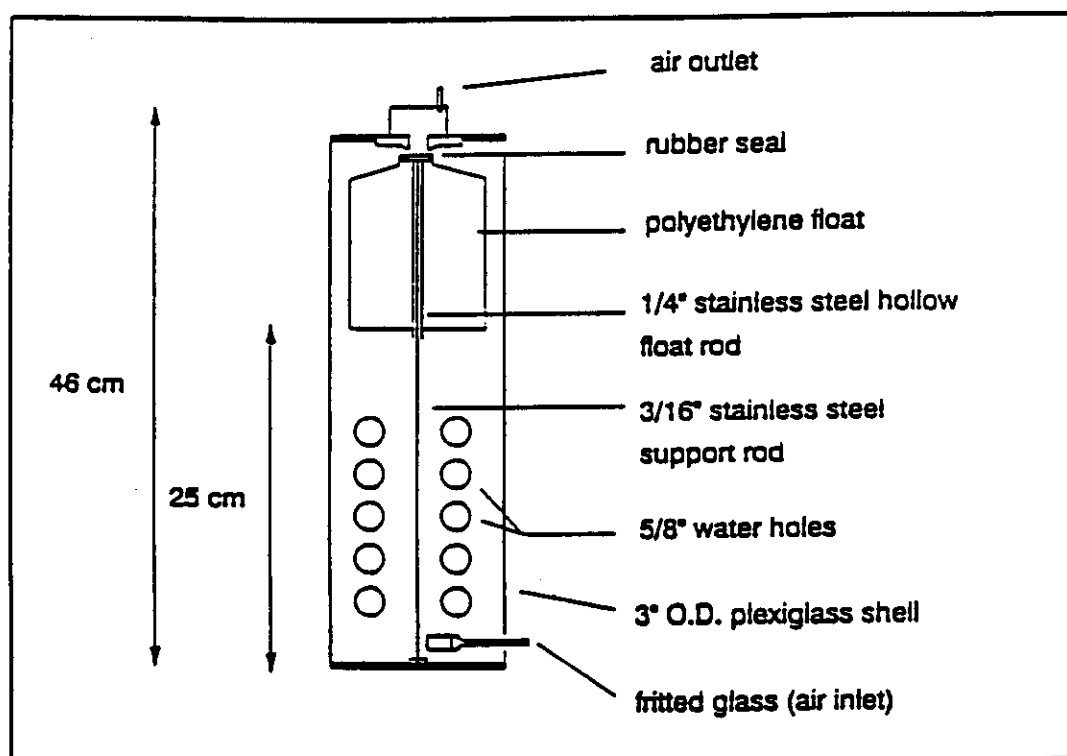


Figure 3.2 Submersible Sparger Design

3.3 System Design and Operation

The prototype submersible sparger was constructed of a clear, plexiglass, shell in order to facilitate experimental observations and the identification of problems. The focal point of the device is a polyethylene float, which is attached to a hollow rod that easily slides along the inner support rod. A rubber seal is located at the top of this float and is intended to help regulate the level of water within the device and prevent liquid contamination of the adsorbent trap, especially as the device is being lowered to a specific depth or raised to the surface.

During normal operation, air is introduced from the bottom of the sparger through fritted glass. These fine bubbles, which behave essentially as rigid spheres, rise through the water column. The turbulent action of the bubbles helps to ensure that the water in the sparger column is well mixed and constantly being replenished through the flow holes, thus providing a representative sample of the surrounding water.

As the bubbles rise, chemical in the water diffuses into the air spaces and approaches equilibrium. These bubbles enter an air chamber near the top of the column where the air is finally introduced through a trap. The "float" is self-regulating. If the volume of air in the vessel increases, the float sinks and the valve opens, allowing air to pass upwards through the trap. As the air volume falls the float rises, shutting off the air flow. In theory, the system can handle any desired air flow at any depth. The chemical is collected by adsorption on to TENAX TA, the adsorbent material in the trap, and the exiting air, which is now free of chemical, is discharged back to the surrounding water. The trap which contains the adsorbed chemical(s), is analyzed to yield the amount of chemical collected and this information is used to determine the chemical concentration in the air, which then can be related to the freely dissolved concentration, using the known air-water partition coefficient for that chemical. It is essential to know the volume of air which has been sparged.

Although there are many factors which affect the operation of the sparger and the accuracy of the results, equilibrium length and mixing within the sparger are two of the most important properties which were investigated. The equilibrium length determination is necessary to assess the length of sparger column required for the chemical to approach equilibrium. Mixing tests can show whether or not the water in the sparger column is being sufficiently replenished.

Tests were also performed which attempted to simulate chemical concentrations present in the water column under a oil slick in order to determine the sensitivity of the device.

3.4 Results and Discussion

Equilibrium Length

The equilibrium length is the minimum length that an air bubble must rise, while in contact with the water , before the concentration of the chemical(s) approaches equilibrium between these two phases. Approach to equilibrium is important because it enables the air-water partition coefficient to be used to determine the freely dissolved concentration of the chemical in the water.

The results of the initial tests show that equilibrium is nearly achieved for bubble column heights as small as 5 cm. This rather short sparging height corresponds to an overall air-water contact time of less than one second which suggests that the transfer of chemical across the air-water interphase occurs very rapidly. It is important to note that these results conflict with some previous work done on floating sparger systems with a different design which suggest a sparging height greater than 20 cm is required to approach equilibrium. However, variations in equilibrium length are expected since this value depends on the properties of the chemical and operating conditions such as water temperature and bubble size.

Mixing

Good mixing of the water within the sparger, through the flow holes, is important to ensure that the chemical being quantified is not depleted from the column as the measurement progresses. Dye was injected into the column to investigate mixing characteristics. The results of these tests confirm that there is more than adequate introduction of water through the flow holes, during normal operation of the device, and hence the sampled water is a good representative of the surrounding environment. Mixing in the column is mostly a result of turbulence caused by the rising bubbles. The observed mixing time was less than one minute.

Operating Considerations

In the eventual field application of the submersible sparger, there will be considerable flexibility in the operation of this device. For instance the question of how outlet air is discharged is an important consideration. Another point is how air is introduced to the sparger. Air can be supplied from the surface by a compressed air cylinder or pump, or it can be introduced from a cylinder attached to the device itself. The mode of operation may be dictated by the type of application, and the desired depth. (Fig. 3.3)

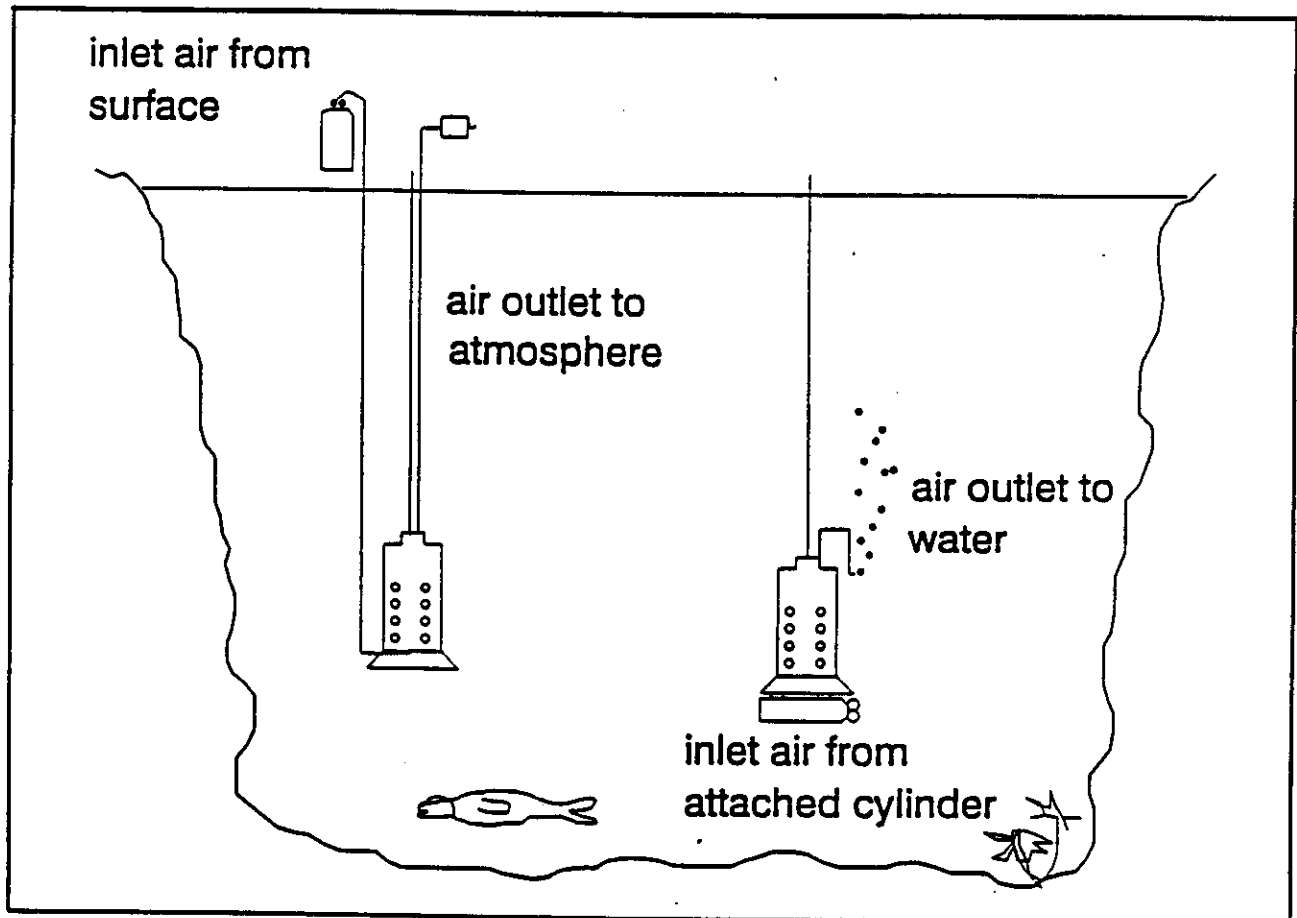


Figure 3.3 Operating Considerations for The Submersible Sparger

The initial tests on the submersible sparger were performed with the outlet air discharged to the atmosphere. This was the desired mode of operation because it allowed direct quantification of the air at the outlet and consequently the volume of air which passed through the trap. However, discharging the air to the atmosphere produces a large pressure drop across the seal and the float/seal assembly becomes critical for proper operation of the device. It must be very reliable to maintain the air space at the top of the sparger column and it may require that the mass of the float must be adjusted depending on the depth of deployment.

It was found that a much simpler method of operating the sparger would be to simply discharge the outlet air to the surrounding water by means of an inverted "U-tube" as shown in Fig. 3.3. The advantage of this approach is that the large pressure drop across the trap is removed and an air space is maintained at the top of the column. The float/seal assembly is no longer critical when operating in this manner, and can even be removed if desired.

Releasing the outlet air to the surrounding water is the preferred method of operating the device but requires that the total volume of air passed through the trap be measured at the inlet. Having a reliable value for the air passed through the trap is necessary to give an accurate calculation for the chemical concentration in air which is related to the water concentration through the air-water partition coefficient, K_{Aw} , as discussed earlier. Therefore, in order to obtain a reliable sample volume it is important that none of the inlet air escapes the system. The most probable losses are through the water flow holes as the bubbles released from the fritted glass begin to spread as they rise up the column. It is possible to avoid this loss by creating lips on the bottom surface of the flow holes, which would guide the rising column of bubbles towards the centre of the sparger. (Fig. 3.4)

The air source for the submersible sparger is another design issue. A compressed air cylinder located on the surface, could easily be used for this purpose. The cylinder would be able to provide air to the sparger even at substantial depths such as 100 m, where the required air pressure would be 10 atm.

A more elegant approach might be to fix a small, compressed air cylinder to the device itself. Although this eliminates the need for a long, cumbersome, inlet hose, it would require a means of turning the air flow on and off and a method of accurately measuring the air volume passed through the trap (for example, by relating it to the pressure drop in the cylinder). Another

option is to discharge the entire known contents of a small air cylinder attached to the device. There is obviously a need to investigate all of these possibilities and design features.

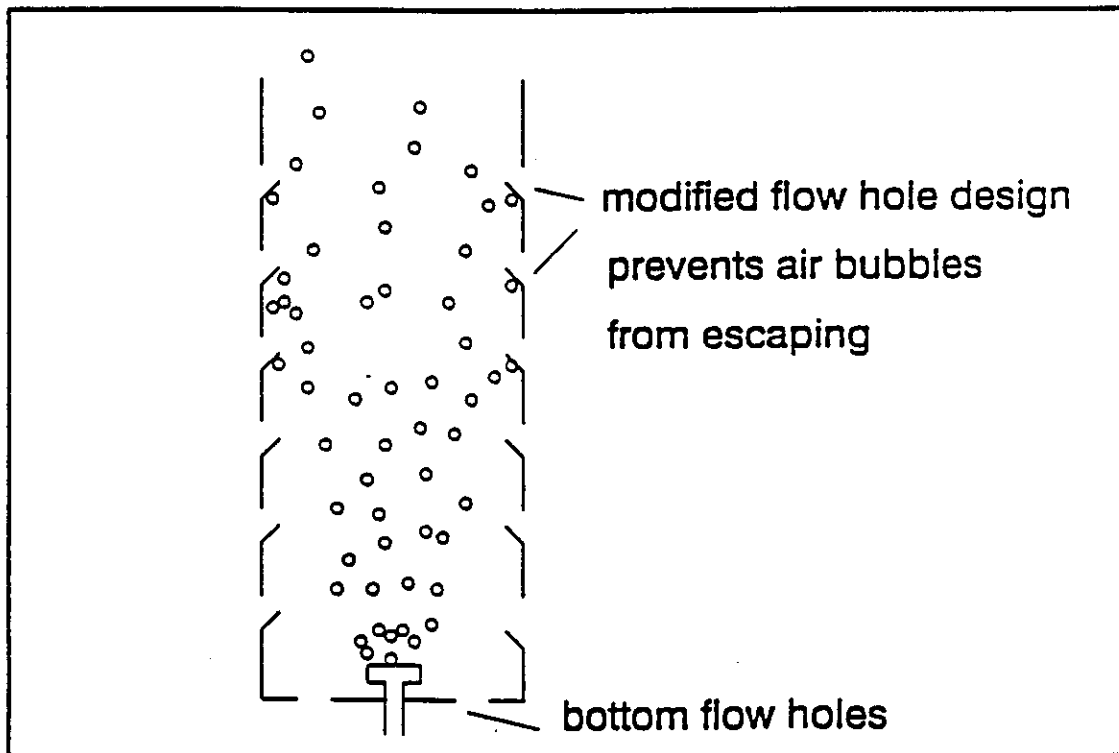


Figure 3.4 Modified Flow Hole Design

Sensitivity To Selected Chemicals and Oil Spill Application

Tests were performed to determine the sensitivity of the sparger to chemicals which would be present in the column of water under an oil slick. A saturated solution of EPS Standard oil in water was diluted 25 times to simulate the chemical concentrations which might be expected. The gas chromatogram of Fig. 3.5 is the result of a 10 minute experiment at an air flow rate of 30 ml/min. It shows that a 300 ml air sample volume is more than adequate to measure the level of contamination in the water column under a slick. Toluene and benzene were

identified as the major components present in the sample.

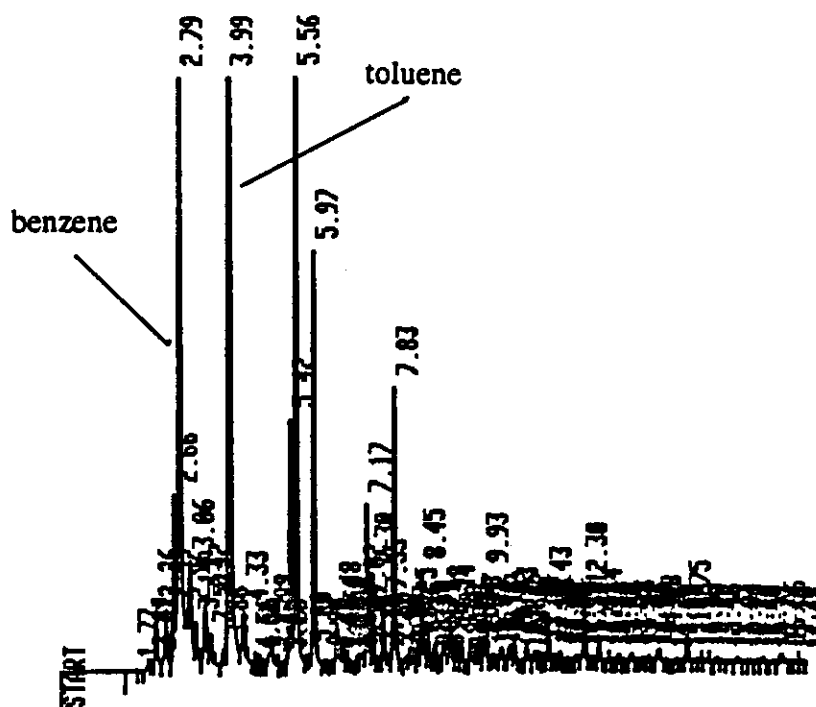


Figure 3.5 Gas Chromatograms of Selected Hydrocarbons

The ability of the prototype submersible sparger to sense and measure very small concentrations of toluene and benzene leads to the possible application of this device in measuring the diffusion of hydrocarbons in the column of water below an oil slick at sea. (Fig. 3.6) Characterizing the diffusion of these chemicals away from the slick is important since this is the major contributor to toxicity in the marine environment. In the event of a spill, the sparging device could easily make a number of measurements in a relatively short period of time which would allow for a fast assessment of the potential danger to marine life. Measurements could also be continued on a long-term basis to study the persistence of these chemicals and their continued influence on the water quality.

The system is regarded as being particularly suitable for deployment at depths in the column of tens of metres, where the concentration of dissolved hydrocarbon is subject to considerable uncertainty. It is well known from previous studies of experimental spills that dissolved hydrocarbons of a few mg/L may extend to depths of a few metres below the slick, but there is concern that some oil may be transported to the benthic region, contaminating valuable shellfisheries. This device is capable of deployment at such depths.

There is an obvious problem of ensuring that the device itself does not contaminate the water by becoming coated with oil during deployment.

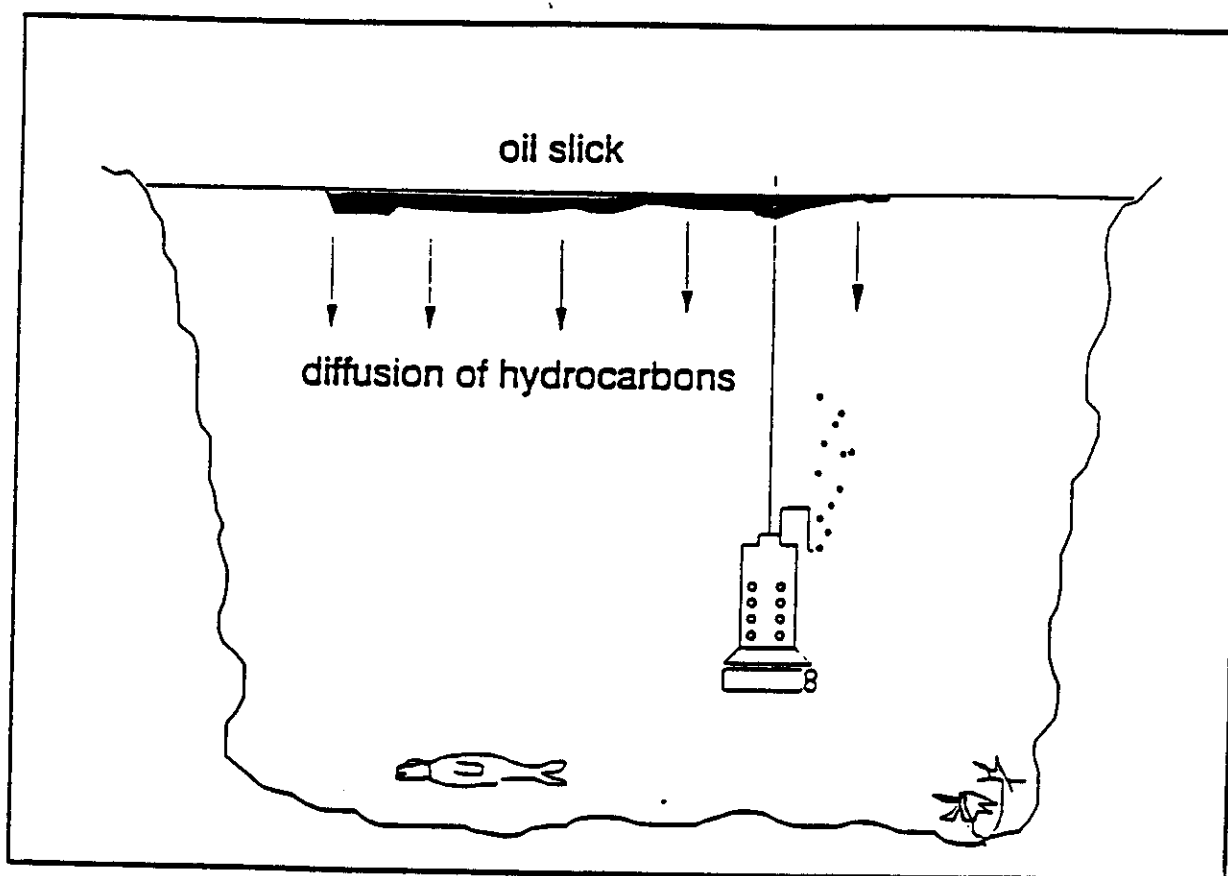


Figure 3.6 Measurement of Hydrocarbons

3.5 Conclusions

A following conclusions were reached concerning the operation of the prototype submersible sparger and its potential application in oil spill research.

1. Dye tests performed on the prototype submersible sparger show that there is sufficient mixing within the sparger column to ensure that the water is being replenished and is representative of the surrounding environment.
2. The equilibrium length data suggests that equilibrium is achieved with hydrocarbons for bubble column heights as small as 5 cm. Therefore, the sparger which has a column height of approximately 25 cm, will certainly provide sufficient air/water contact time for equilibrium to be approached.
3. The preferred method of operating the device is by discharging the outlet air to the surrounding water by means of a valve or inverted "U-tube". However, more work needs to be done to investigate the different variations in operating the submersible sparger.
4. Because of the sparger's success in detecting low concentrations of hydrocarbons, it is believed that this device has potential for measuring the extent of diffusion of hydrocarbons in the column of water below an oil slick, and hence characterizing the adverse effects of such spills on the marine environment.

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